Photochemical Modeling of Atmospheric Ozone

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Proposed Activities:

1. *Polar Ozone:*
   - 1.1 Validation of SAGE III Estimates of Chemical Ozone Loss
   - 1.2 Testing Consistency Between Measured and Modeled Chemical Ozone Loss Rates

2. *Mid-Latitude Ozone:*
   - 2.1 Validation and Analysis of SAGE III NO_2 and NO_3
   - 2.2 Testing the Bromine Budget of the Lowermost Stratosphere
   - 2.3 Inferring HO_2 from Measurements of NO_2, HO_2NO_2, and H_2O_2

1.1 Validation of SAGE III Estimates of Chemical Ozone Loss

Three "primary" methods for estimating chemical loss of ***ozone column***:

a) Tracer-tracer correlations
b) "Match"
c) vortex average descent

Good agreement for SOLVE/THESEO 2000 Arctic winter among the three techniques:

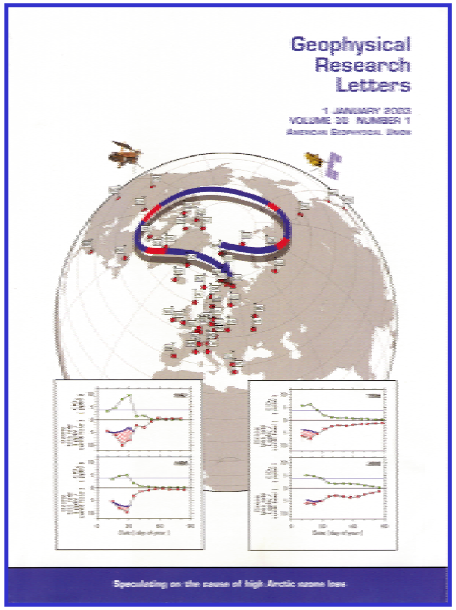
Tracer-Tracer : Salawitch *et al*., JGR, 2002
Match : Rex *et al*., JGR, 2002
Vortex Average Descent: Hoppel *et al*., JGR, 2002

See Table 3-2, "Polar Ozone" chapter, WMO 2002

Proposed Activities:

- Ozone loss using tracer-tracer correlations (MkIV, Geophysica, ILAS II) & Match for SOLVE-2/EUPLEX Arctic winter & future Arctic winters → ***well underway!***
- Ozone loss comparisons for first "Match" Antarctic campaign in 2003
- Ozone loss for future winters using tracer-tracer correlations from ILAS II, ACE, and future aircraft campaigns

1.2 Testing Consistency Between Measured and Modeled Chemical Ozone Loss Rates



1. Models can not account for full extent of measured chemical loss, particularly for cold Arctic Januaries

Rex, Salawitch, Santee, Waters, Hoppel, & Bevilacqua, "On the unexplained stratospheric ozone losses during cold Arctic Januaries", *GRL*, 1 Jan 2003.

2. Revised ClO and ClOOCl from SOLVE campaign is prompting a rexamination of key kinetic parameters:

Salawitch, Stimpfle, Wilmouth, Anderson, & Canty, "ER-2 Measurements of ClO and ClOOCl: Implications for Theory and Observation of Ozone Loss", EGS/AGU, April 2003.

Proposed Activities:

- Use of SAGE III OClO to constrain BrOx, ClOx, and kinetic parameters → ***details to soon follow!***
- Examination of SAGE III *measured* loss rates during periods of solar illumination at consistently high SZA (e.g., Arctic January, Antarctic August) versus *modeled* loss rates

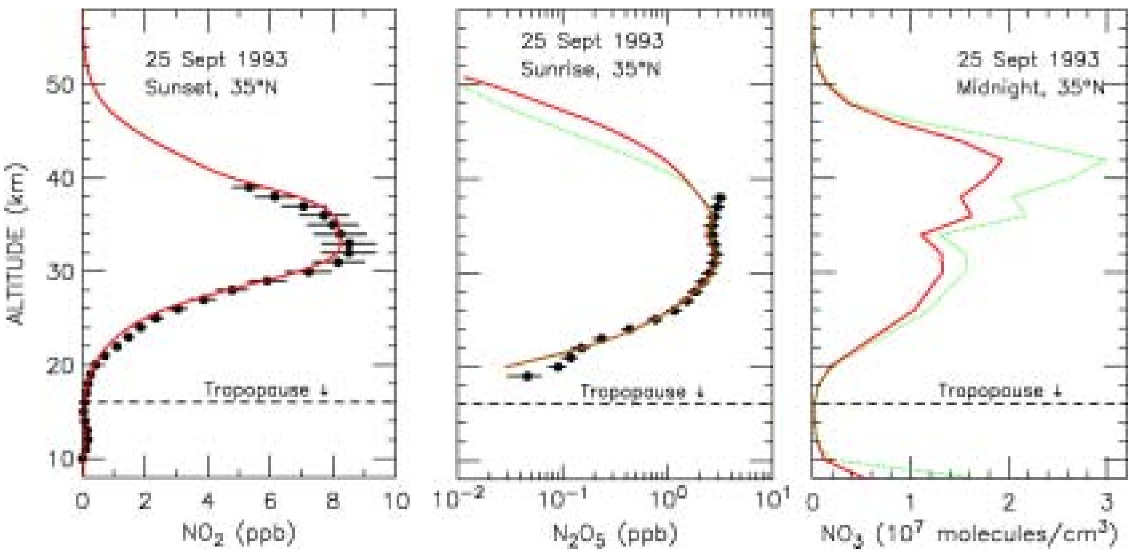
2.1 Validation and Analysis of SAGE III NO_2 and NO_3

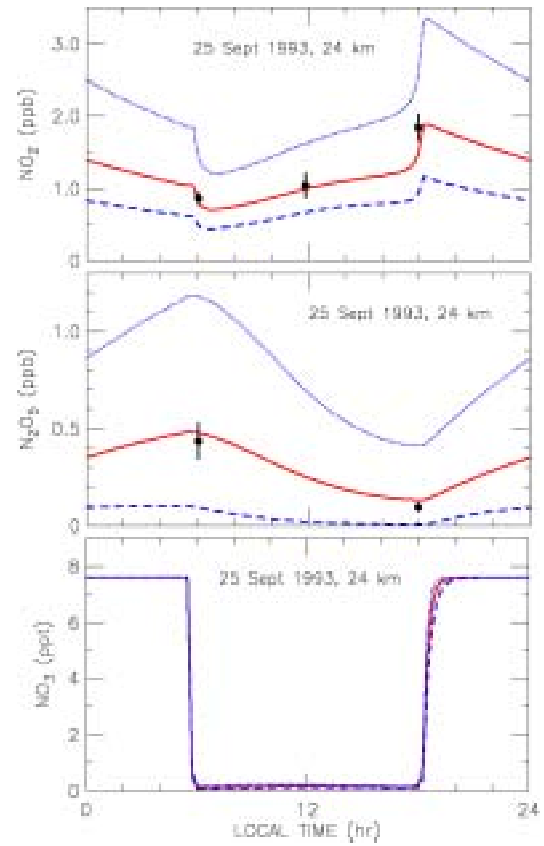
1. Constrained photochemical model useful for:

- Calculating profiles of NO_3 consistent with measured NO_2 (SAGE III, MkIV, ILAS II)
- Using balloon data collected at sunrise to validate satellite data obtained at sunset (e.g., 1 April 2003 MkIV flight)

RED SOLID : JPL 2000 Kinetics
BLUE DOTTED : 30 × Background Aerosol Loading
BLUE DASHED : No Heterogeneous Chemistry

RED SOLID : JPL 2000 Kinetics
GREEN DOTTED : Changes to N_2O_5 thermal decomposition and k_{NO2+O3} suggested by Aliwell & Jones, GRL, 23, 2589, 1996





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2. Proposed Activities:

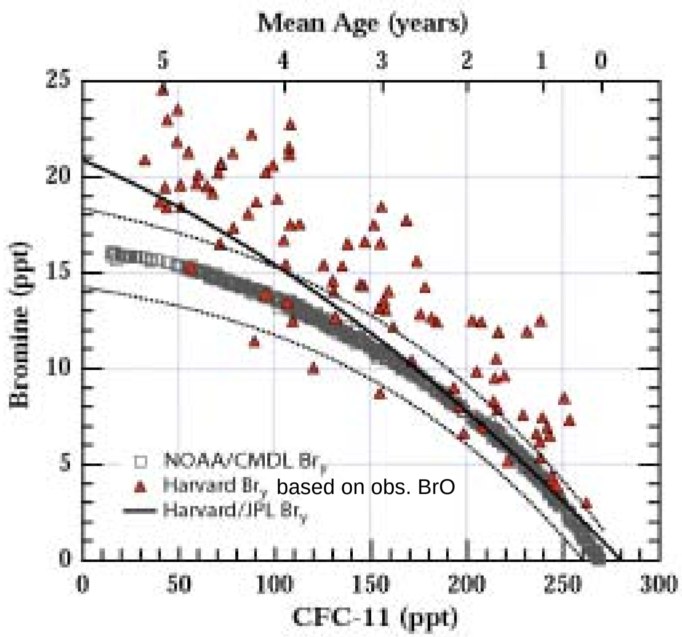
- Photochemical model simulations in support of validation of SAGE III NO_2 and NO_3
- Examination of SAGE III NO_2, H_2O, and extinctions for evidence of heterogeneous sinks of NOx on cold aerosol and sub-visible cirrus (e.g., Keim et al., *GRL*, *23*, 3223, 1996) as well as volcanic aerosol in the event of a major eruption
  $\rightarrow$ lunar data (extends into tropics) & sunrise SH solar data (mid-latitudes)
- Examination of NO_2 profiles from ACE, ILAS II, and SCHIAMACHY for heterogeneous sinks in the lowermost stratosphere

2.2 Testing the Bromine Budget of the Lowermost Stratosphere

1. Motivation

- Models driven by observed changes in chlorine and bromine fail to fully account for the large downward trends observed for O_3 in the lowermost stratosphere (LMS)
- SOSST groups will continue to define dO_3/dt in the LMS
- Various observations suggest either VSL (very short lived) organics or BrO in the upper troposphere result in much more BrO in the LMS than found by standard models

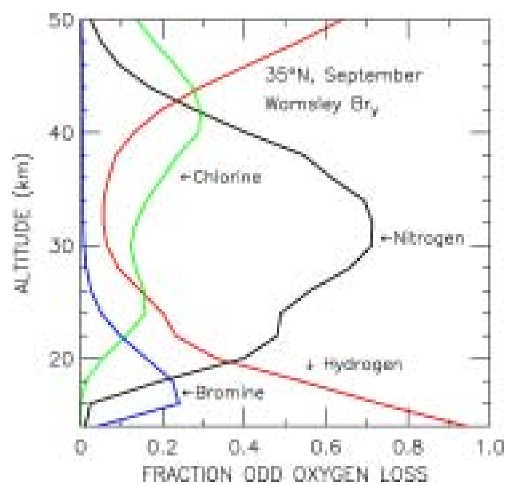
~4 pptv must be added to "standard" Br_y vs CFC-11 relation to match observed BrO in the LMS



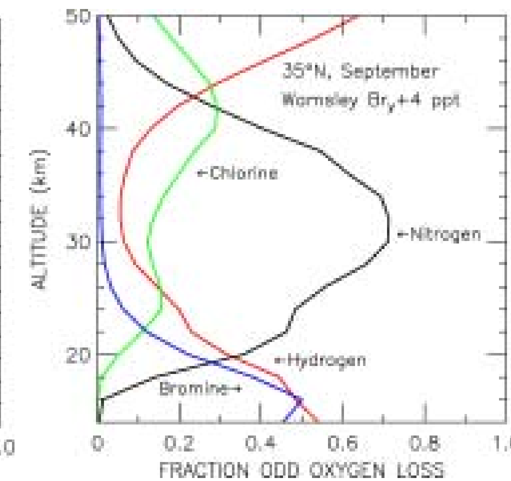
Wamsley *et al.*, *JGR*, *103*, 1513, 1998

This change to the Br_y vs CFC-11 relation dramatically alters the cycles that control O_3 in the LMS

"Standard" Br_y vs CFC-11



Br_y+4.0 ppt vs CFC-11



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2. Proposed Activities:

- Analysis of bromine budget in the LMS using profile and column data from GOMOS and SCHIAMACHY
- Data from aircraft, DOAS, and MLS also important
- Relate findings to observed ozone trends in the lowermost stratosphere

Please see Chapter 2, WMO/UNEP 2002 (Ko & Poulet *et al.*), available on-line at:

http://www.wmo.ch/web/arep/reports

for an excellent discussion of the scientific issues involving the fate of VSL brominated compounds.

2.3 Inferring HO_2 from Measurements of NO_2, HO_2NO_2, and H_2O_2

1. Motivation

- HO_2 plays a key role in the photchemisty of the lower stratosphere (LS) and the upper troposphere
- Global observations of HO_2 in the LS and UT have never been obtained

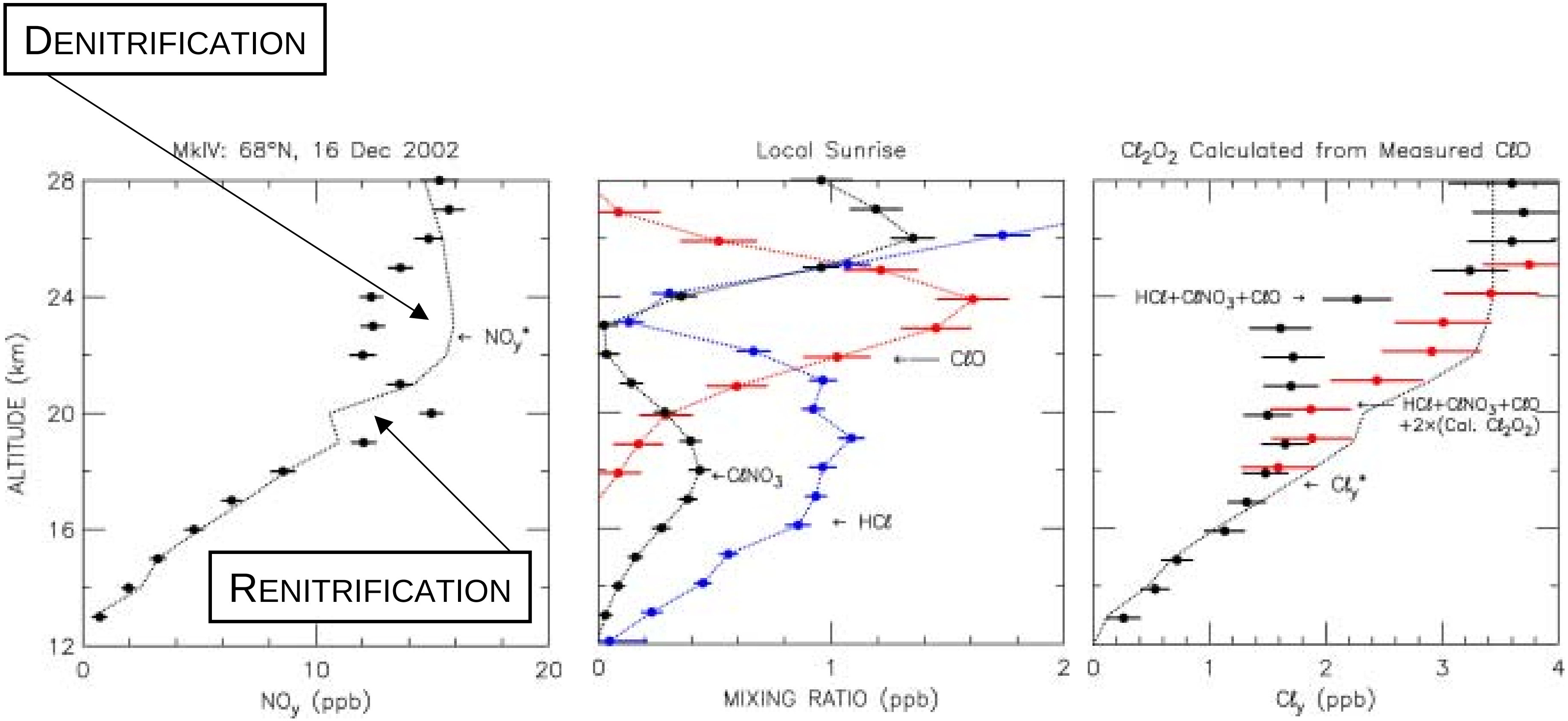
2. Recent Advances

- Demonstration of quantitative consistency between models and measured H_2O_2 (MkIV and FIRS 2) based on a new lab rate for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (Christensen *et al*., GRL, 2001GL014525, 2002)
- Demonstration of quantitative consistency between modeled and measured HO_2NO_2 (MkIV), HO_2 (ER2), and NO_2 (ER2) based inclusion of near IR photolysis of HO_2NO_2 in the model (Salawitch *et al*., GRL, 2002GL015006, 2003)

3. Proposed Activities:

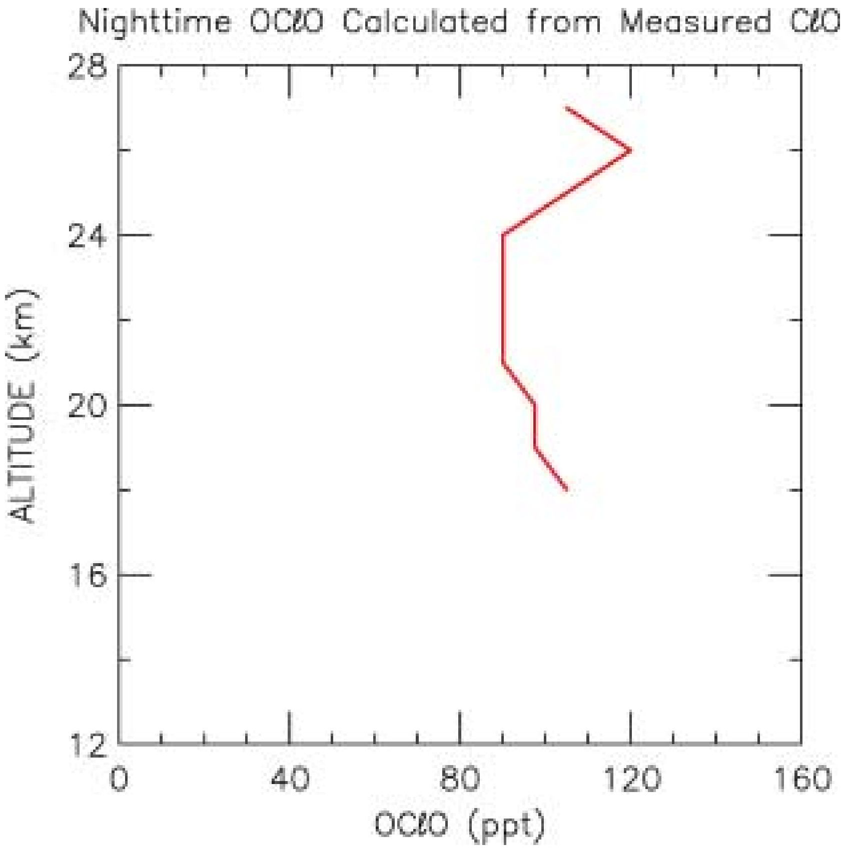
- Exploratory investigation of “reconstruction” of global fields of HO_2 from solar occultation measurements of NO_2, HO_2NO_2, and H_2O_2 (MIPAS and ACE)
- Evaluation of the validity of “reconstructed HO_2” based on comparison to aircraft data

MkIV Flight, 16 Dec 2002

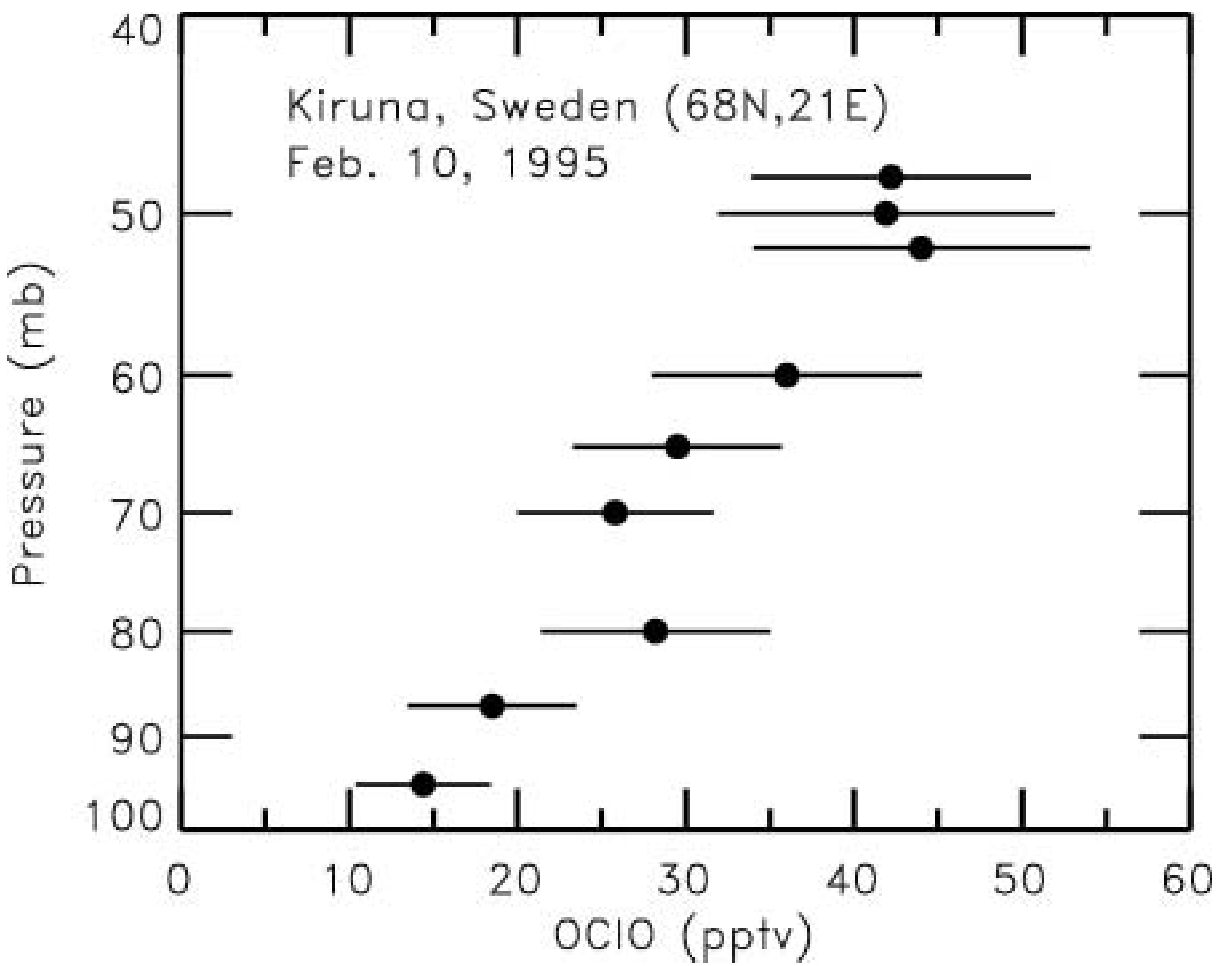


- Vortex became very cold, quite early
- Denitrification & elevated ClO observed mid-December 2002

MkIV Flight, 16 Dec 2002



Nighttime OClO Measurement

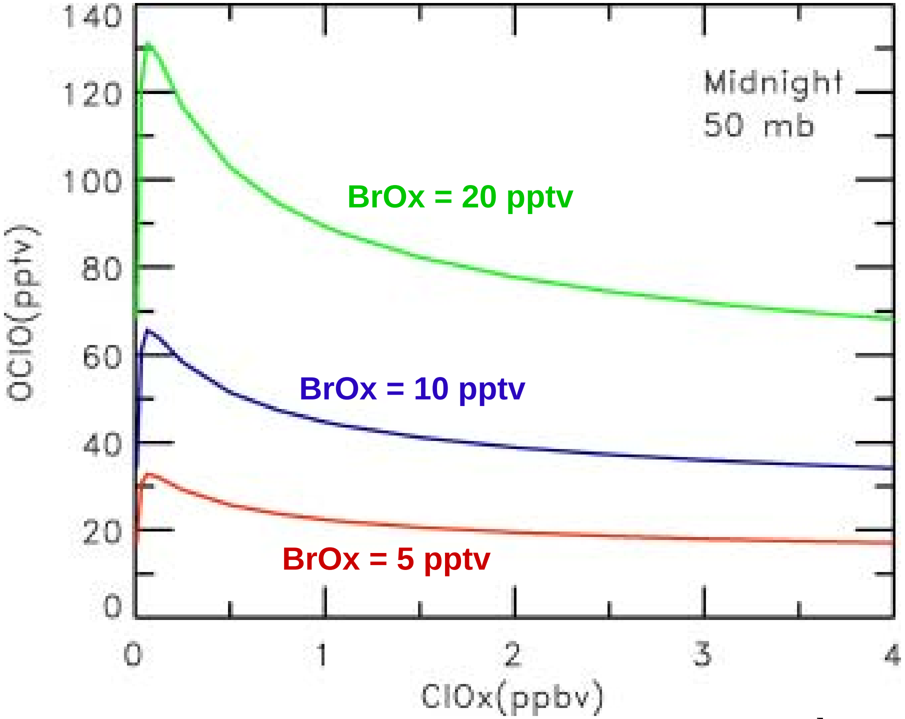


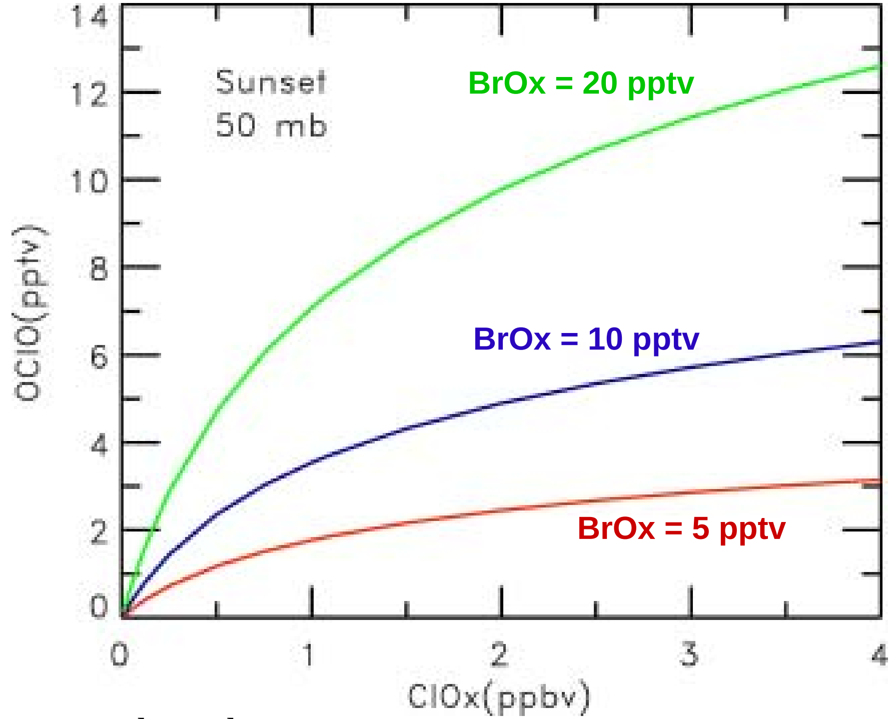
Renard *et al., JAC, 26*, 65, 1997.

Nighttime & Twilight OClO

Nighttime OClO is a function primarily of BrOx for activated vortex

Twilight OClO is a function of BrOx and ClOx, particularly for observed levels of BrOx (~20 pptv)



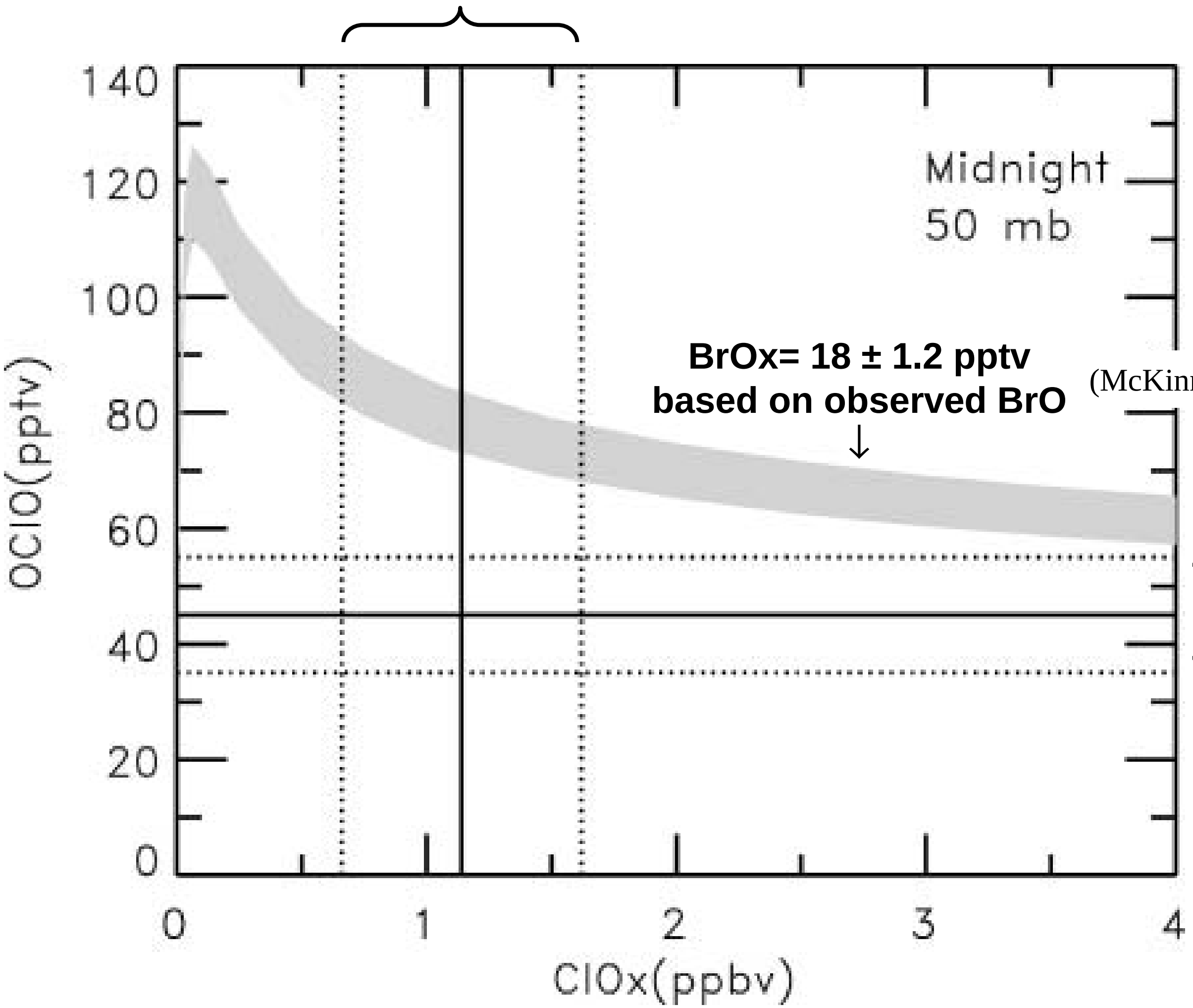


ClOx = ClO + 2 × ClOOCl

BrOx = BrO + BrCl

OClO versus BrCl yield

ClOx based on observed ClO by MLS for Feb 1995



(McKinney in situ BrO and Pfeilsticker DOAS BrO)

Observed OClO, midnight, 10 Feb 1995
Renard *et al.*, JAC, 26, 65, 1997

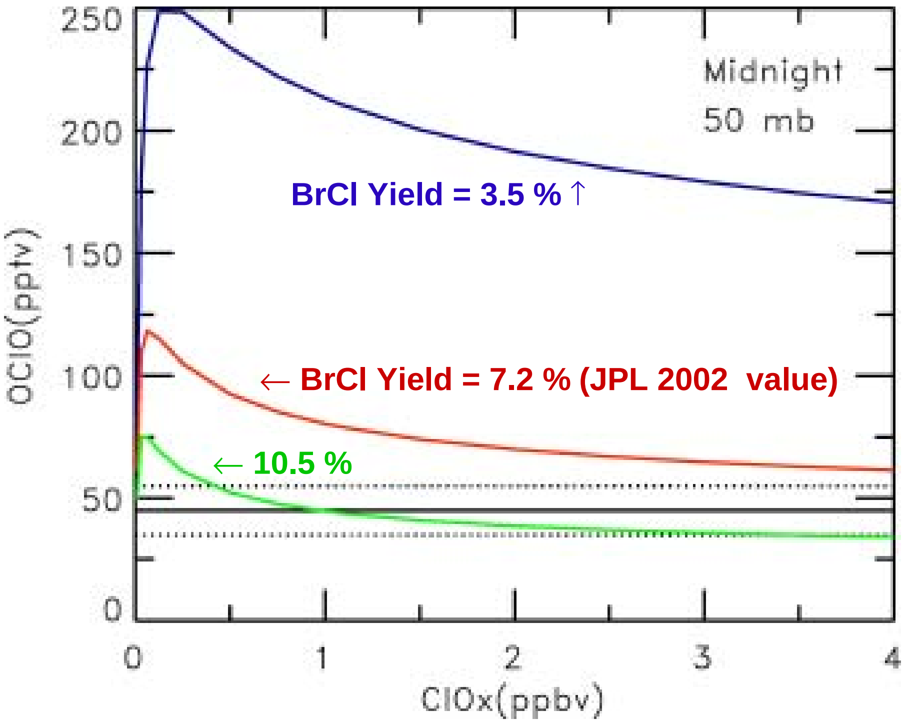
$ClOx = ClO + 2 \times ClOOCl$

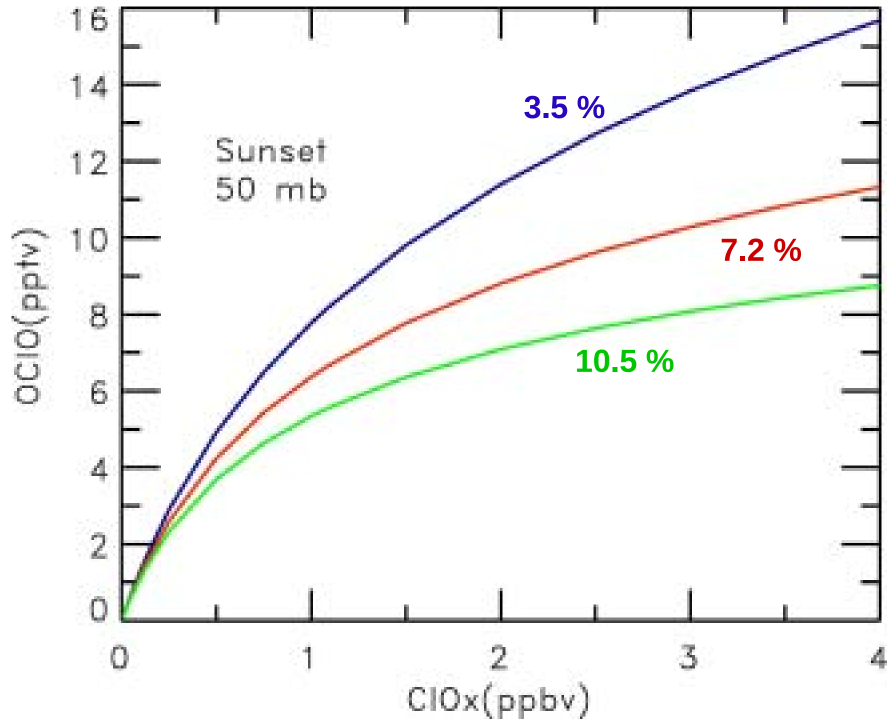
$BrOx = BrO + BrCl$

OClO versus BrCl yield

- BrOx = 18 pptv (observed) used for all model runs
- Yield of BrCl from BrO + ClO indicated:

$$BrO + ClO \rightarrow BrCl + O_2$$
$$\rightarrow OClO + Br$$
$$\rightarrow ClOO + Br$$





Nighttime OClO is much more sensitive to the yield of BrCl from the BrO + ClO reaction than is twilight OClO

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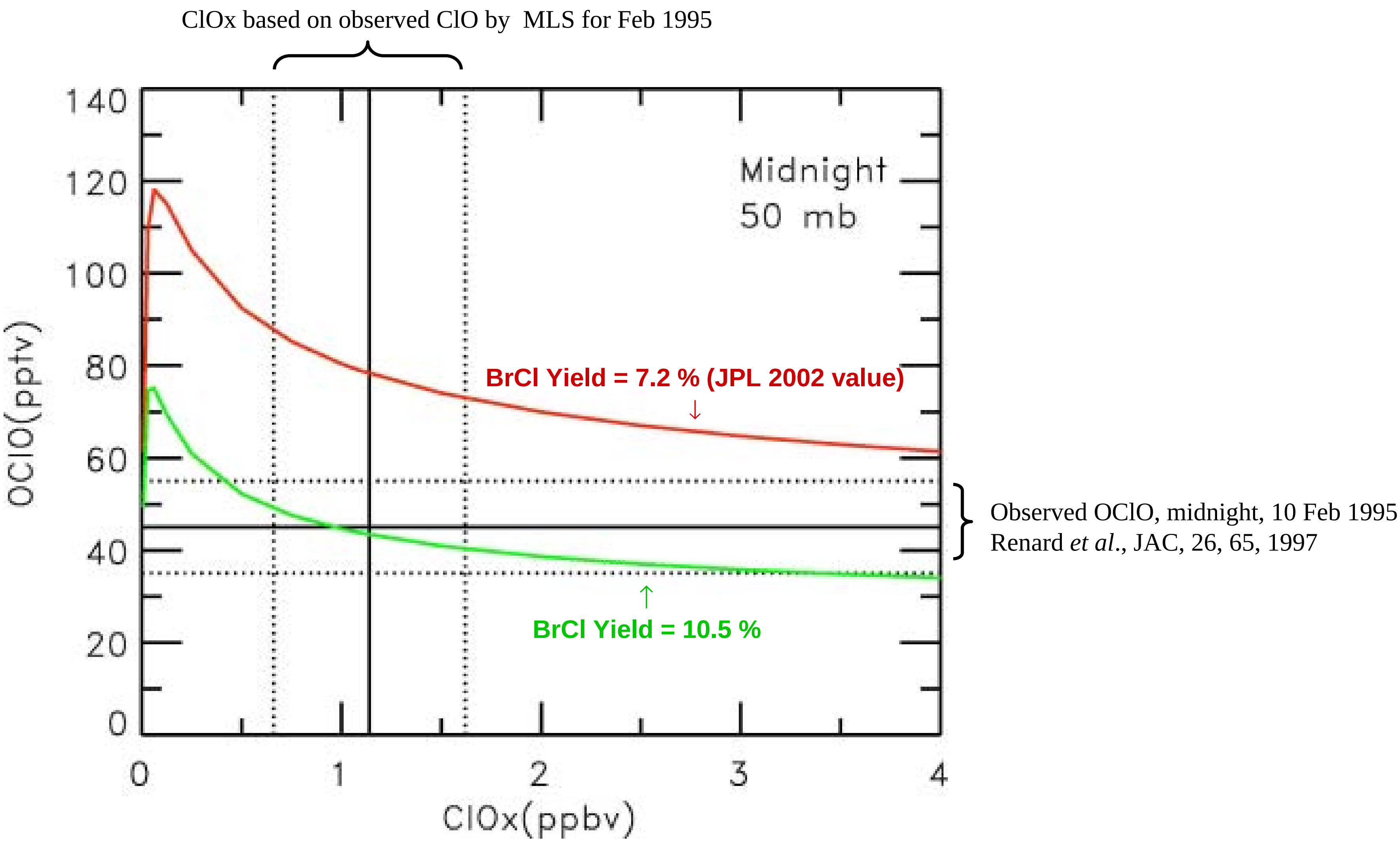
$$
\begin{aligned}
BrO + ClO &\rightarrow BrCl + O_2 \\
&\rightarrow OClO + Br \\
&\rightarrow ClOO + Br
\end{aligned}
$$



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&\rightarrow ClOO + Br
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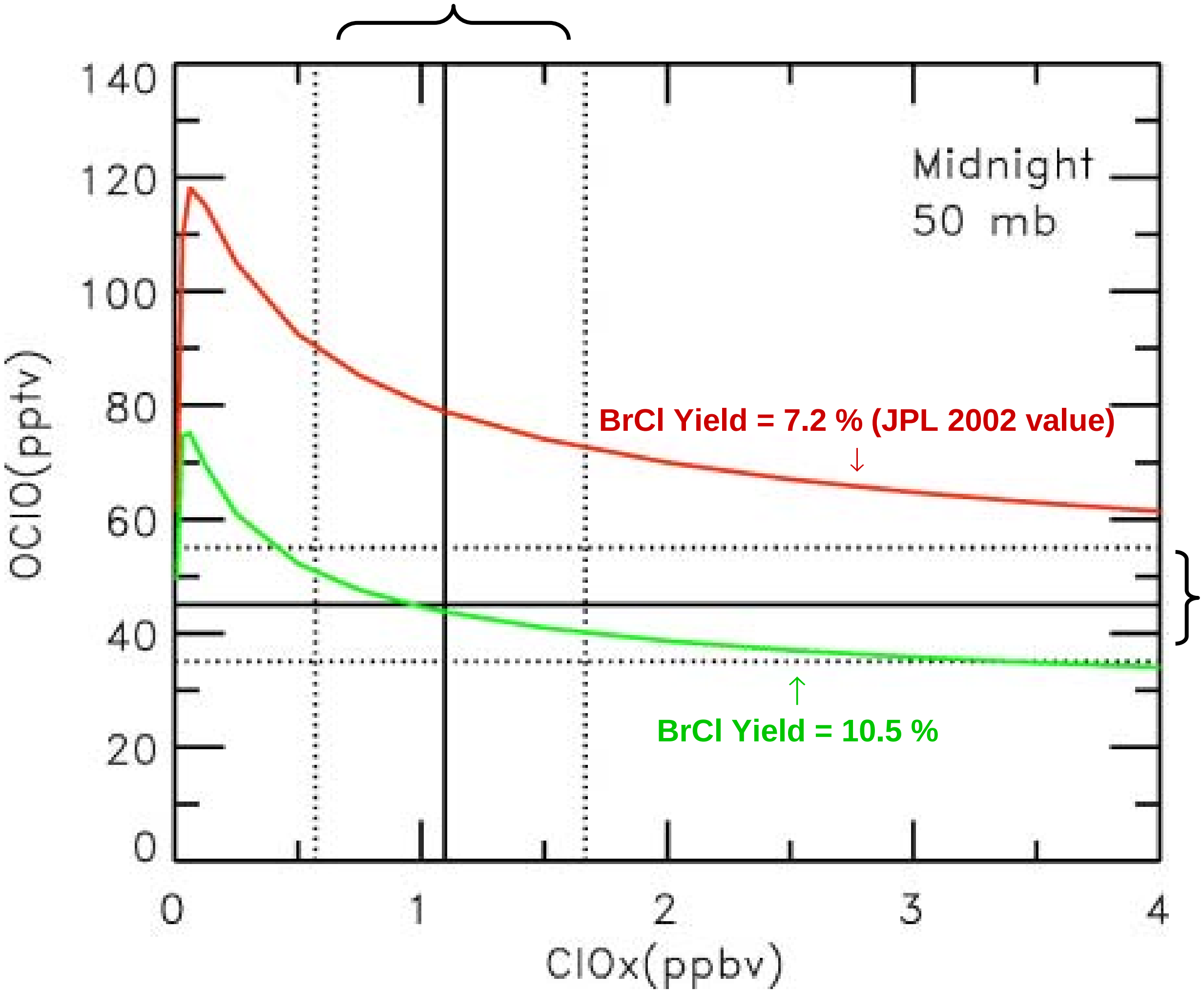
$$

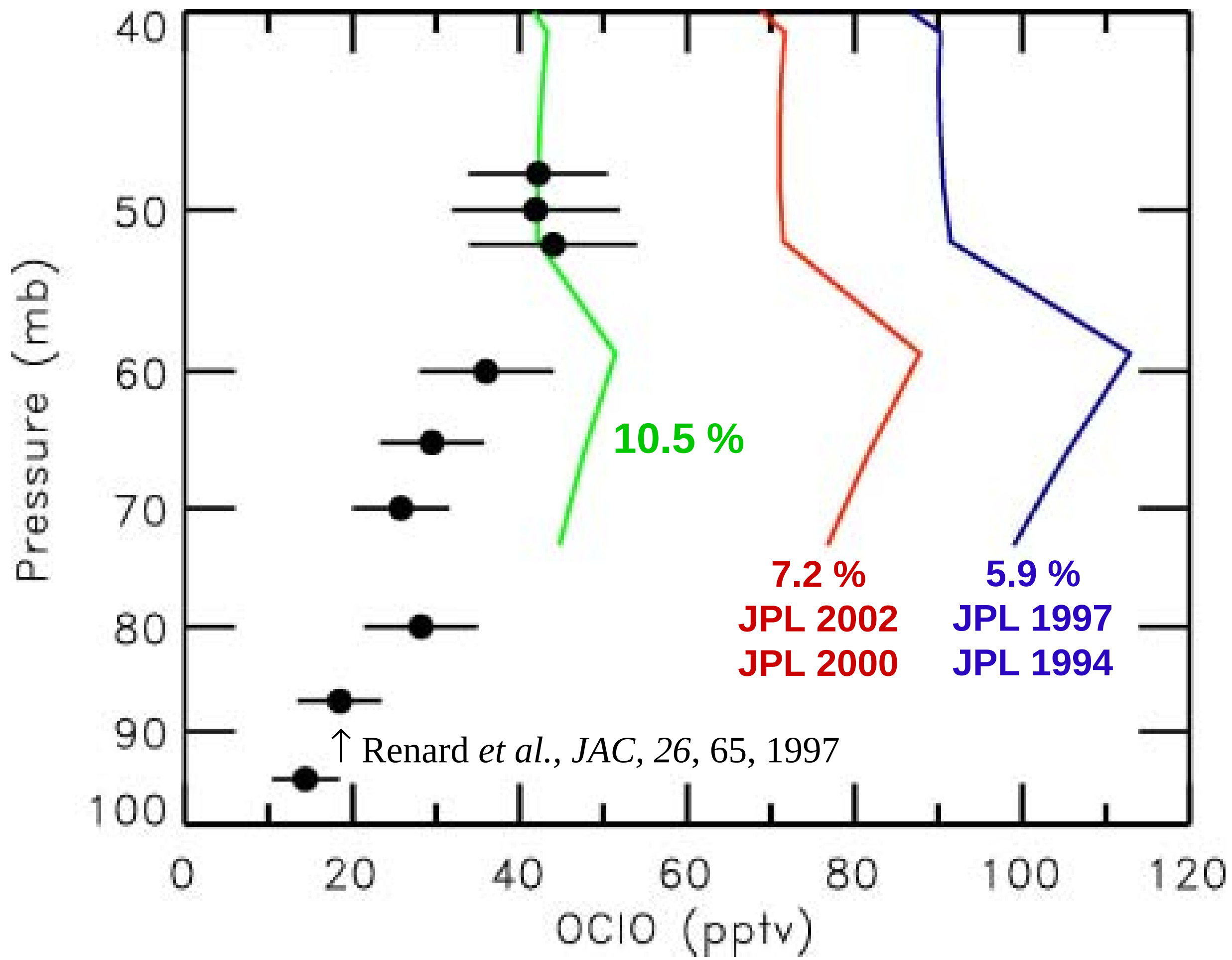
ClOx based on observed ClO by McKinney *et al.* for Feb 1995



Observed OClO, midnight, 10 Feb 1995
Renard *et al.*, JAC, 26, 65, 1997

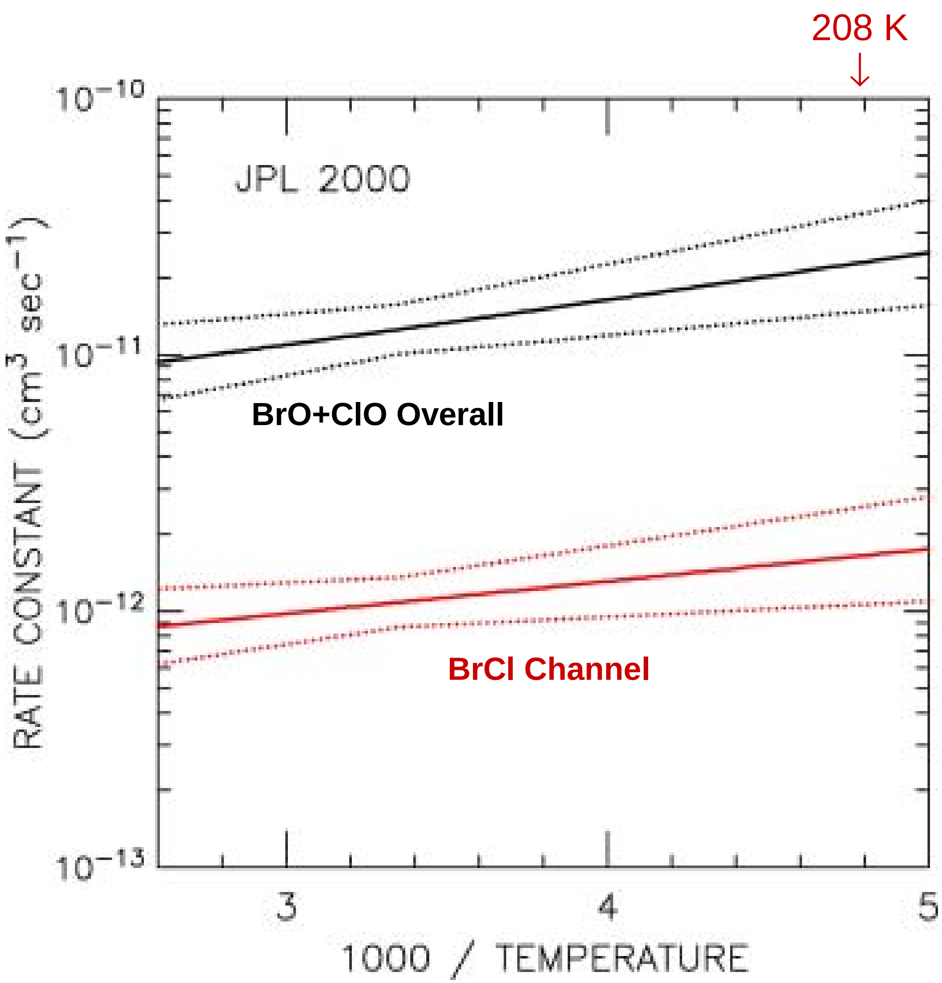
Nighttime OClO Measured and Modeled

Model constrained by measured profiles of
ClO & BrO in Arctic vortex for Feb 1995
(McKinney *et al.*, *GRL*, 24, 853, 1997)



Is a 10% yield of BrCl realistic ?

Yes, if uncertainties are considered:



BrCl Yield =
7.2 ± 3.0 % (T=208 K)

Note:
Lab studies conducted to 220 K;
values at lower T based on extrapolation.

Final Comments

Nighttime OClO of great interest for:

- geographic extent of ClOx activation
- abundance of BrOx in the polar stratosphere

However, quantitative use of these data requires understanding how nighttime OClO is affected by branching of the BrO+ClO reaction

Ancillary constraints on ClOx and BrOx (e.g., data from MkIV; data from EUPLEX) will be important for initial interpretation of SAGE III OClO

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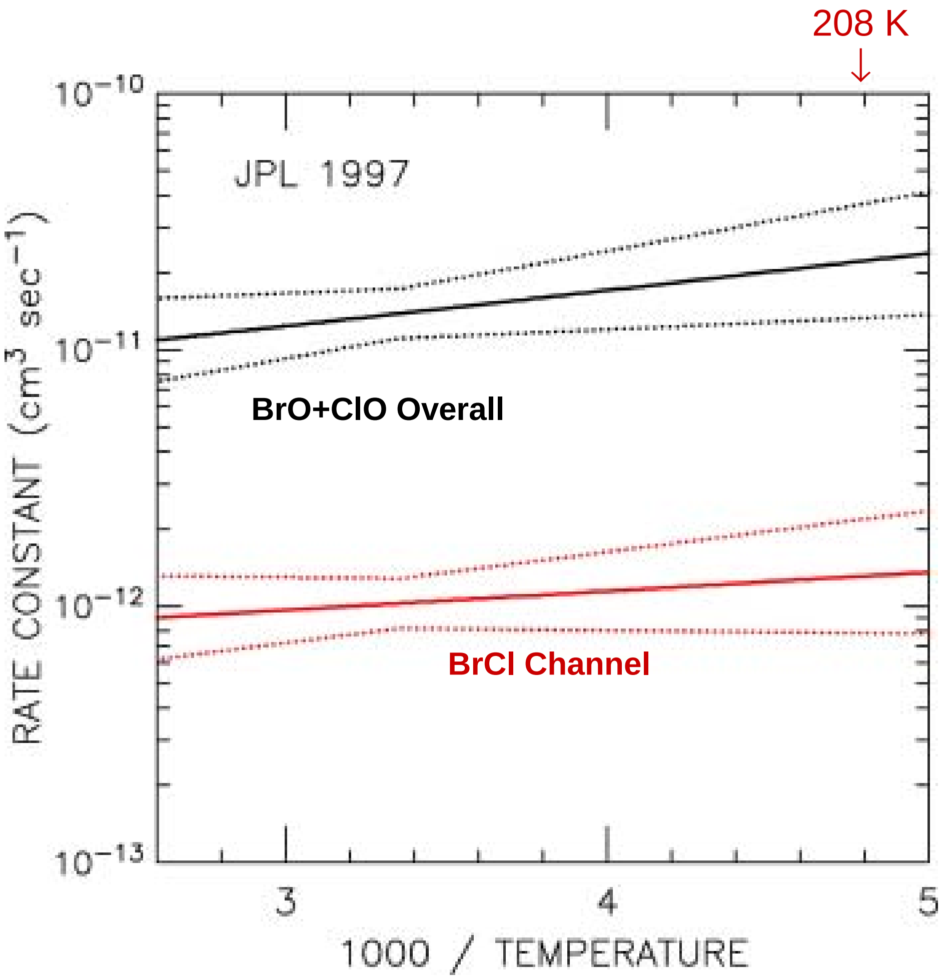

BrCl Yield =
5.9 ± 3.3 % (T=208 K)

Note:
Lab studies conducted to 220 K;
values at lower T based on extrapolation.

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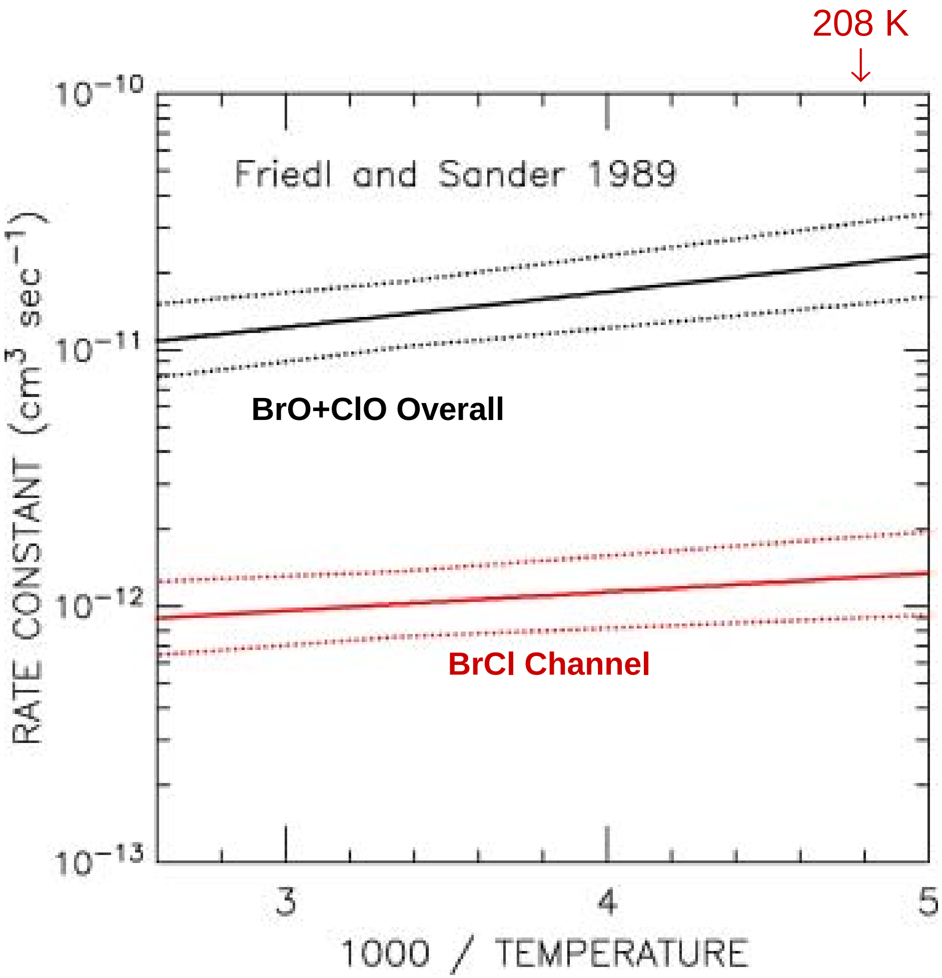

BrCl Yield at 298 K:
Friedl & Sander 1989 : 7.4 ± 2 %
Poulet et al. 1990 : 12 ± 5 %

BrCl Yield =
5.9 ± 2.0 % (T=208 K)

Note:
Lab studies conducted to 220 K;
values at lower T based on extrapolation.